

Reactive Surfactants in Heterophase Polymerization. XVI. Emulsion Copolymerization of Styrene–Butyl Acrylate–Acrylic Acid in the Presence of Simple Maleate Reactive Surfactants

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ABSTRACT: This study deals with the influence of a copolymerizable surfactant on the stability of lattices. Two main reactive surfactants, one anionic and one nonionic, both containing a reactive part issued from maleic anhydride, were engaged in seeded emulsion polymerizations of styrene-*co*-butyl acrylate-*co*-acrylic acid. The importance of the polymerization conditions clearly appears through the incorporation yield of the surfmers: When good conditions are used, this yield can be as high as 80%. Once stable lattices are synthesized, with a great incorporation of the surfactant, the stability of the colloid (against freeze–thawing cycles or in the presence of concentrated divalent electrolyte solutions) is then largely improved. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2768–2776, 2000

Key words: styrene–acrylic copolymers; emulsion polymerization; reactive surfactants; maleate derivatives

INTRODUCTION

This series of articles is devoted to the use of reactive surfactants in heterophase (mainly emulsion) polymerization. Many arguments have already been given to show the potential interest of such surfactants in the synthesis of film-forming lattices¹ and this has been the object of a cooperative work of seven laboratories, supported by the European Union. The main purpose of this group is to study the behavior of this kind of surfactants and try to optimize their structure in order to obtain the best performance in the polymerization and the result-

ing properties of the films in the potential applications.

Among the criteria which have to be considered, the incorporation of these surfactants at the surface of the particles is certainly the major one. In this respect, a maleate anionic derivative has been shown to be quite interesting (see Part VII² and VIII³ of this series). However, another very important criteria is the accessibility of the chemical (ease of preparation), while another fact of growing importance is the environmental friendly character of the surfactant molecules.

The purpose of the present article was to report the results obtained with two maleate compounds: one anionic and one nonionic, which correspond to the last two criteria mentioned. Their behavior in seeded emulsion polymerization is compared with that of the well-known sodium dodecylsulfate (SDS).

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EXPERIMENTAL

Materials

Styrene (Prolabo, Paris), butyl acrylate (Prolabo), and acrylic acid (Aldrich, Paris) monomers are commercial products and are used with no further purification (acrylic acid) or after distillation under reduced pressure (styrene and butyl acrylate). The initiators are either potassium persulfate (KPS) or 2-2'-azobis[2-methyl-N(2-hydroxyethyl)-propionamide] are commercial products (Aldrich and ref. VA86 of Wako Chemical) and both are water-soluble.

The half-ester of maleic anhydride (HEC12), or monododecylmaleate, and its oxylated derivative were obtained according to ref. 4. HEC12 is obtained simply by heating equimolar amounts of maleic anhydride and dodecylalcohol in the melt (80°C) and then recrystallizing from heptane. A catalytic ethoxylation⁴ was used to obtain the ethoxylated derivative with 32 or 41 ethylene oxide units. The catalyst was a silica-supported aluminum alcoholate and the polymerization of ethylene oxide was carried out at room temperature, followed by a treatment at 45°C.

On the other hand, a commercial (Aldrich) monomethyl ether of poly(ethylene glycol) with 45 ethylene oxide units was reacted with either maleic anhydride or HEC12 upon heating at 80°C in a toluene solution, in the presence of catalytic amount of *p*-toluene sulfonic acid. The initial solution of the ether was dried upon the reflux of toluene in a Dean and Stark apparatus. After reaction, the toluene solution was precipitated upon addition of ethyl ether at -20°C. The products were finally filtered and dried overnight at room temperature under a vacuum.

Surface Tension Measurements

The measurements were carried out in water solutions at 20°C, using a Kruss K12 apparatus, and working with a DUNOY ring.

Cloud-point Measurements

A differential turbidimeter, built in the laboratory, was used. The temperature was controlled in between 20 and 100°C. A 1% w/w solution of surfactant was used in presence of MgSO₄ at a concentration 0.33*N*.

Emulsion Polymerizations

Polystyrene Seed

Styrene emulsion polymerization was carried out in batch conditions at 70°C, using the following

recipe: water 1500 g, styrene 170 g, KPS 1.1 g, Na₂S₂O₅ 1.0 g, and SDS 2.3 g. After 3 h reaction, the monomer conversion was complete and the latex was washed as follows: It was diluted by deionized water at 1% solid contents and treated with a mixture of ion-exchange resins. Every 2 h, the latex was filtered and its conductivity was measured. Further amounts of ion-exchange resins were introduced and the process was repeated until the conductivity remained constant. The washed latex was then concentrated at 10% solid contents and stored in polyethylene containers.

Model Core-Shell Lattices

After some trials, the following protocol was carried out to obtain film-forming core-shell lattices, without either flocculation or renucleation: From a seed particle size of 100 nm, the amount of monomers was calculated so as to obtain monodisperse particles of 200 nm in diameter. The initial charge was water 390 g, seed latex 300 g (at 10% solid content), styrene 1.45 g, butyl acrylate 1.48 g, acrylic acid 0.03 g, SDS 0.83 g, and KPS 1.7 g. Then, a semibatch was carried out with two streams of liquids feeded during 400 min. The first stream contains a mixture of monomers as follows: styrene 82 g, butyl acrylate 83.5 g, and acrylic acid 1.7 g. The second stream contains SDS, 2.84 g, in solution with 40 g of water.

The polymerization temperature was 65°C, and after a feeding period of 400 min, the process was continued for 200 min (postpolymerization) so that the final conversion was higher than 95%. The basic protocol was also used upon replacing SDS by reactive surfactants, with some modifications if needed.

Latex Characterizations

The particle size was analyzed by dynamic quasi-elastic light scattering (DQELS; Malvern Autosizer). Molecular weight of the polymer was determined by size-exclusion chromatography, on the basis of polystyrene standards. Surface tensions were carried out from the final latex.

The incorporation yield of the reactive surfactant was obtained from NMR measurements on the washed latex (Bruker, 250 MHz) for the non-ionic surfactant, from a comparison of the protons from the poly(ethylene oxide) units ($\delta = 3.7$ ppm) and from the styrene units ($\delta = 7$ ppm) (the δ are expressed from tetramethylsilane). In the case of

HEC12 (nonionic surfactant), which does not contain ethylene oxide units, the area covered by HEC12 was estimated from the difference between the critical micellar concentration (c.m.c.) (as measured by surface tension method or by conductimetric titration) of SDS in pure water and in the presence of a given amount of washed latex.

Stability Tests

The washed lattices were submitted to freeze-thaw cycles, according to the following method: A small amount (≈ 3 g) of latex was cooled at -20°C during 30 min and then reheated at room temperature. After the ice melting, the sample was gently agitated and the particle size was measured. If the particles did not coagulate, the operation was carried out again. The latex's solid content was either 1% or 10% w/w.

The stability in salt (monovalent NaCl and divalent MgSO_4)-water solutions, at 2 mol L^{-1} , was also studied. In this case, an equivalent volume of the latex and water solution was melted and agitated, so that the real salt concentration was 1 mol L^{-1} . Then, the particle size was measured and compared to that of the initial latex.

To study the lattices' stability in ethanol, a drop of washed latex was put into pure ethanol. The particle size in ethanol was measured by DQELS. Moreover, the ethanol was replaced by water, and the redispersability was also studied by DQELS measurements.

RESULTS AND DISCUSSION

Surfactant Synthesis

The synthesis of HEC12 is straightforward. The yield after recrystallisation is 93% with a melting point of 59°C .

The condensation of poly(ethylene glycol) monomethyl ether is also an easy reaction carried out at 80°C with a twofold excess of maleic anhydride. However, a part of the maleic anhydride was reacted twice, so that POE-maleate-POE compounds can be formed. From $^1\text{H-NMR}$ and SEC measurements, it can be estimated that $2/3$ of the product has the monomaleate structure and $1/3$ of the final product presents the bis-POE structure (molecular weight 400 g mol^{-1}). In both the cases of HEC12 and POE maleate products, no isomerization in fumarate was observed. The

condensation of the same product [poly(ethylene glycol)monomethyl ether] onto the HEC12 is a little more difficult and needs the presence of a catalytic amount of *p*-toluene sulfonic acid to be completed after 12 h, again at 80°C .

In the catalytic polymerization of ethylene oxide initiated by HEC12, the initial aluminum alcoholate bond of the catalyst is replaced by an acylate bond, until the initial alcoholate residue of the catalyst is liberated as an alcohol. After the first insertion of one ethylene oxide units, the bond to the catalyst is restored as an alcoholate bond and then a rapid exchange between the alcohol and the catalyst may take place. As soon as all the HEC12 molecules have been reacted with the catalyst, and then with the first ethylene oxide molecule, all the HEC12 moieties will be chain ends of a living ring-opening polymerization of ethylene oxide. High yields of polymerization (such as 90%) are obtained after 4 h and almost complete conversion of the ethylene oxide engaged is reached after 12 h. It should result in a narrow Poisson distribution, but, unfortunately, the SEC analyses are perturbed because some residue of the catalyst support cannot be fully separated and some disaccordances are observed between the molecular weight deduced from $^1\text{H-NMR}$ and the values measured by SEC (for instance, 1395 instead of 1690 g mol^{-1} for a product containing 32 ethylene oxide units).

Micellar Properties of the Surfactants

The micellar properties of the surfactants are determined through surface-tension measurements, from which it is possible to obtain their c.m.c., as well as the area covered by each surfactant molecule onto polystyrene latex. Figure 1 shows a typical curve of $\text{C}_{12}\text{MOE}_{32}\text{-OH}$. In Table I, the data are reported, including the c.m.c., the surface tension above the c.m.c., and the area covered by one molecule, both onto polystyrene latex (Al) and at the air-water interface (A_s). The data A_s can be deduced from the Gibbs Duhem⁵ equation:

$$A_s = \frac{10^{20}}{N_a \Gamma}$$

where N_a is the Avogadro number and Γ is proportional to the slope of the plot between γ and $\text{Log } C$ (C = concentration):

$$\Gamma = \frac{1}{RT} \frac{d\gamma}{d(\text{Log } C)}$$

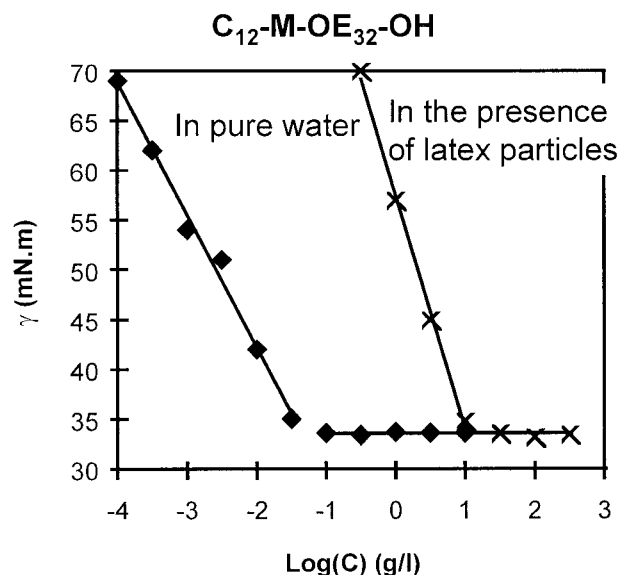


Figure 1 Surface-tension measurements in pure water or in the presence of polystyrene latex particles for $C_{12}\text{-M-OE}_{32}\text{-OH}$.

In such conditions, A_s is given in $\text{\AA}^2/\text{molecule}$. Moreover, the cloud points, as measured by the turbidimetric method, are also reported in Table I.

There is no slight difference between the equilibrium surface tension in pure water or in the presence of a polystyrene latex. The anionic reactive surfactant displays a much larger c.m.c. than that of the three nonionic surfactants. The value of the latter are in line with typical nonionic ethylene oxide surfactants.

However, it may be surprising to see the difference between the compound containing the methylic end group and those issued from POE—OH. The hydrophobicity from the methyl end group seems to compensate the hydrophilicity of about 10 ethylene oxide units. This result was quite different from that expected from the so-called HLB balance (hydrophilic-lipophilic bal-

ance), as calculated from the increments proposed by Davies and Rideal.⁶ In fact, according to this scale, the number of ethylene oxide units which compensate the CH_3 group should be only 3. In the same way, the effect of the CH_3 group is also quite important on the cloud-point values.

Model Core-Shell Lattices

The recipe used for producing the seed latex of 100-nm diameter gives quite reproducible results. After having been washed with ion-exchange resins, the latex becomes quite sensitive to flocculation, because its stabilization is just due to the sulfonate charges fixed through the redox initiator system. In such conditions, the stability of the washed seed latex is quite sensible to an ionic strength increase. On that latex, the area covered by SDS was measured as $60 \text{\AA}^2/\text{molecule}$, a value slightly higher than the value given in the literature,⁷ that is, $43 \text{\AA}^2/\text{molecule}$.

The targeted final latex was expected to be a stable latex, coagulum free, with a particle size of 200-nm diameter and, at last, film-forming at room temperature. Then, the composition of the shell to be added to the core was fixed, so that its glass transition temperature, T_g , was about 20°C . It was also important to have a monodisperse particle size and, thus, avoid any renucleation during the feed process.

To keep the composition constant, and without drift (which should occur if a batch process was used), it was decided to use a feed process in starving conditions, so that the instantaneous conversion remains as high as possible and not smaller than 80%. The amount of monomers was calculated to obtain a final particle diameter of 200 nm.

Concerning the choice of the initiator, KPS is expected to increase the ionic strength, and because the stabilization of the washed seed latex is electrostatic with a limited density of charges,

Table I Properties of the Different Surfmers

Reactive Surfactant	HEC ₁₂	$C_{12}\text{M-OE}_{32}\text{-OH}$	$C_{12}\text{M-OE}_{41}\text{-OH}$	$C_{12}\text{M-OE}_{45}\text{-CH}_3$	$\text{M-OE}_{45}\text{-CH}_3$
c.m.c. (g L^{-1})	1.67	0.03	0.13	0.03	—
c.m.c. (mol L^{-1})	5.9×10^{-3}	1.8×10^{-5}	6.2×10^{-5}	1.4×10^{-5}	—
$\gamma_{\text{c.m.c.}}$ (mN m^{-1})	32	33.5	33	28	—
A_s ($\text{\AA}^2/\text{molecule}$)	60	30	53	30	—
A_l ($\text{\AA}^2/\text{molecule}$)	72	35	40	37	—
Cloud point ($^\circ\text{C}$)	—	65	76	66	>100

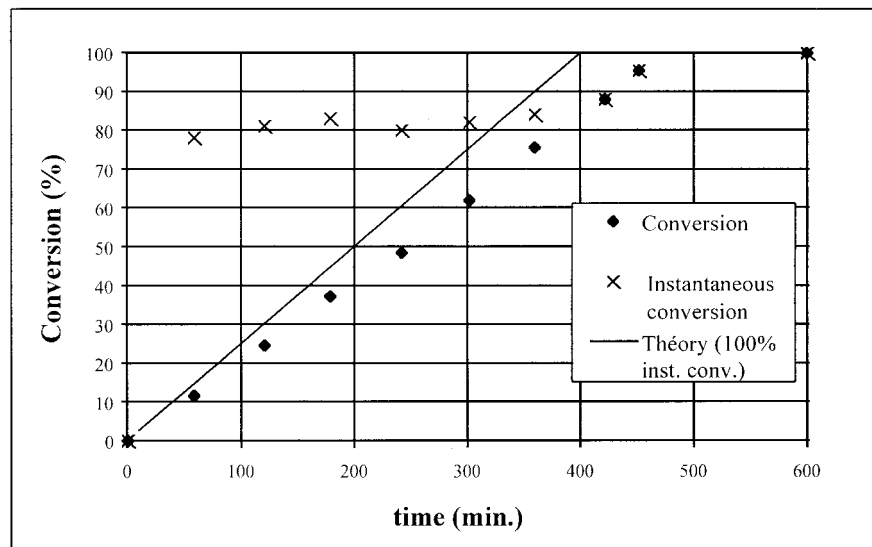


Figure 2 Conversion versus time plot showing the global conversion, compared to the theoretical global conversion, and the instantaneous conversion, in the case of the model core-shell latex.

there is some danger of flocculation. On the other hand, with a nonionic initiator, such as VA86, these stabilizing charges (carried out by the seed particles) may be buried into the growing particles, so that a lack of stabilization should also occur. Then, it was decided to use KPS, but to add it slowly in a feeding process of a water solution.

Finally, to stabilize the latex particles during their growth, the water solution also contains some SDS. This SDS is added in two parts: a small part in the batch with a small amount of monomers (then, the coverage of the seed particles was about 50%, in the surface, of the full coverage). The second part is added with the KPS, at the same rate as that of the main feed of monomers (i.e., 400 min of addition) and the amount of added SDS was calculated in order to synthesize fully covered final particles. The final recipe is then as given in the Experimental section.

The results with such a recipe are given in Figures 2 and 3, as plots of conversion (whole conversion and instantaneous conversion) versus time and particle size versus time. One can see that the instantaneous conversions are such that there is practically no composition drift. The final conversion is 99.5% and the final size is 200 nm, as expected. This represents a ratio between the core and shell of 1/8 (in volume). At last, high molecular weights ($M_n = 135,000 \text{ g mol}^{-1}$) are obtained. For this latex, the area covered by SDS

is $155 \text{ \AA}^2/\text{molecule}$, much larger than for the seed, probably due to the effect of the acrylic acid which very much increases the polarity of the surface.

Core-Shell Lattices with the Anionic Reactive Surfactant

The HEC12, as well as the acrylic acid, were neutralized using NaHCO_3 as a buffer, with a molar fraction of 1.5 versus the whole acid contents. Then, the pH of the final latex is around 5, which is a little bit higher than the $\text{p}K_a$ of the acids.

Taking into account that the surfactant is able to cover 177 \AA^2 for each molecule, it was possible to calculate the theoretical surface coverage of the final latex particles. A first run was carried out on the basis of the recipe of the model core-shell lattices, except that a rather large amount of surfmer was added (enough to cover more than twice the final surface area) before the semibatch feeding stops. A stable latex resulted, with a solid content of about 10%, but with a bimodal particle-size distribution (80 and 150 nm); it was clear that some renucleation took place.

In a second run, a smaller amount of surfmer was used (calculated for 80% of the final area) and it was introduced just during the semibatch feed (the polymerization started in surfactant-free conditions). The solid content was increased to 17%, but, then, flocculation occurred at the very

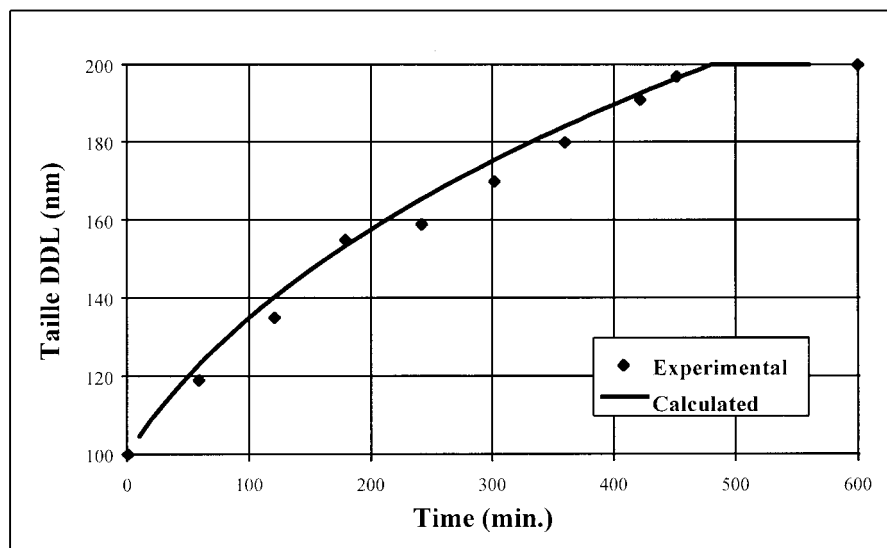


Figure 3 Particle diameter (in nm) versus time plot in the case of the model core-shell latex.

beginning of the feeding process. It was supposed that this flocculation was induced by a too large increase of the ionic strength, so that a further run was carried out using VA86, instead of KPS. However, even in such initiating conditions, a small amount (3%) of coagulum was produced at the end of the feeding period.

Two other trials were more satisfactory and resulted in monodisperse stable lattices of 200-nm diameter and without any coagulum. The conditions used for these runs are reported in Table II. The experimental coverage was obtained as follows: The final latex is first washed, using ion-exchange resins, as described for the seed latex in the Experimental section. In these conditions, only the grafted surfactant remains at the surface of the particles. Then, conductimetric titration was carried out, using SDS (see Fig. 4). By comparison with pure water, a difference in the c.m.c. of the SDS was noted. From that difference,

and knowing the area covered by each SDS molecule (155 \AA^2), as well as the total surface area of the particles, it is possible to calculate the area actually covered by the grafted surfmer. Then, taking into account the area that each surfmer molecule is able to cover (177 \AA^2), the incorporation yield, at the surface, can be obtained, assuming that there is no difference in the area covered by a grafted molecule of HEC12 and the area covered by an adsorbed molecule (177 \AA^2).

The lattices from these two runs are quite stable. For example, when they are submitted to the ethanol test, which causes some flocculation, or at least a rather large increase of particle size (going from 200 to 450 nm), they can easily be redispersed in pure water (particle size becomes again a 200-nm diameter). It is not the case of the model core-shell latex produced with SDS (its size goes from 200 to 330 nm in ethanol and stays at 330 nm after redispersion in pure water).

Table II Core-Shell Lattices with HEC₁₂

Run	Surfmer Amount ^a		Calculated Coverage (%)	Experimental Coverage (%)	Incorporation Yield (%)	Surface Tension (mN m ⁻¹)
	Initial (%)	Feed (%)				
1	0.5	1.5	105	68	56	54
2	0.38	1.14	80	70	75	68

^a Based on the monomer content.

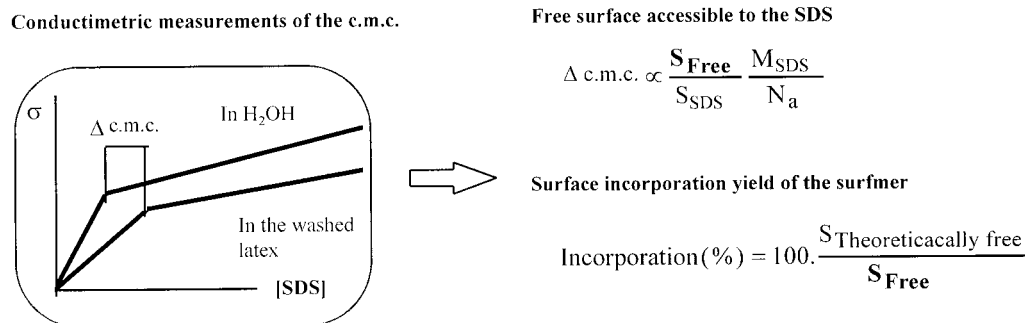


Figure 4 Determination of the half-ester incorporation yield.

Core-Shell Lattices with Nonionic Surfmers

The macromonomer maleate of poly(ethylene glycol) methyl ether is not a surfactant, but it should be able to copolymerize with the monomers engaged in the feed system and then to graft onto the surface of the particles. This should result in "hairy" latex particles, and in a stable latex, if the poly(ethylene oxide) moieties are long enough to give a good steric stabilization.

Rather large amounts of a macromonomer are needed so as to produce the actual surfactant by copolymerization as soon as possible (and then to stabilize the particles). To avoid flocculation due to a high ionic strength, VA86 was used as an initiator, instead of KPS. Moreover, a small amount of SDS (0.10 g) was introduced before the feeding process. Using 4.7% (w/w, versus the monomer content) of the macromonomer, it was possible to obtain a stable latex, with 17% solid content, a particle size of 200 nm, and a final conversion of 99%.

The washing process includes, first, ion-exchange resins, in order to separate the SDS mol-

ecules, and then a long ultrafiltration process with from 20 to 50 times the initial volume of the serum after dilution to 1% solid content. After washing, the latex can be concentrated up to 15% solid content, and its surface is then 71 mN m⁻¹. The incorporation yield was then determined by ¹H-NMR, as mentioned in the Experimental section. This yield was shown to be 30%.

Another series of experiments, reported in Table III, were carried out in the presence of nonionic surfmers. The calculated amount, taking into account the data of Table I (concerning the surface coverage on a polystyrene latex), was very large and was reduced by a factor of 3–6. The grafting yield, as measured by NMR, indicates that the incorporation of the reactive surfactant is far from complete. The largest amount of the surfactant is recovered as water-soluble compounds (either monomeric unreacted surfactant or oligocopolymers) upon centrifugation of the latex. Another part of the surfactant is just adsorbed onto the latex surface, but may participate in the stabilization, as well as the grafted surfactant. After

Table III Core-Shell Lattices with Nonionic Reactive Surfactants

Run	Acrylic Acid (%)	Surfmer (%) ^a	No. Ethylene Oxide Units	Solid Content (%)	Amount of Surfmer		
					Grafted (%)	Adsorbed (%)	Water (%)
1	0	8.4	32	10	28	15.5	56.5
2	1	8.4	32	10	33	15	48
3	1	4.2	32	10	48	16	36
4	1	4.2	32	18	55	—	—
5	1	4.2	41	10	35	—	—
6	1	0.8 + 3.4	45	15	50	—	—
7	1	0.8 + 2.2	45	20	70	—	—

^a Based on the monomer content.

washing (using ultrafiltration, as described above), it remains as grafted (or eventually buried) reactive poly(ethylene oxide) moieties. The results reported in Table III confirm, first, that acrylic acid is important to increase the apparent reactivity of the surfmer, because it is water-soluble and favors the homogeneous polymerization in water. As shown by entries 1 and 2 of Table III, the incorporation yield goes from 28 to 33%.

Other parameters are also effective: Decreasing the amount of the surfmer causes also an increase of its incorporation yield up to 48%, while the amount of just-adsorbed species remains about constant. The adsorbed species are thought to be mainly co-oligomers and, then, it appears that the amount of the reacted surfmer is the higher when its concentration is smaller. Finally, a further increase in the incorporation yield can be obtained by increasing the solid contents of the latex, probably because the surface available for adsorption of the surfmer has been increased.

On the other hand, as shown by comparing runs 3 and 5, upon increasing the hydrophilicity of the surfmer [using a surfactant with a longer poly(ethylene oxide) chain], the incorporation yield is decreased. In all the runs from 1 to 5, the surfmer has been introduced in one step.

In the last two runs, the surfmer has been introduced again in two steps, as for the model core-shell latex. Its structure was also modified: The methyl end group replaced the OH end group. In fact, this allows one to use a longer POE chain (which is good for providing an increase of stability, as shown in a previous study⁸), without increasing the hydrophilicity. Moreover, the fact to introduce a part of the surfmer in a semibatch feeding process causes the maleate compound to react later; this fact tends to increase its incorporation and also avoids burying it. Upon comparing runs 6 and 7, the higher incorporation yield in run 7 is due to two things: a decrease of the whole amount of the surfmer and an increase of the final solid contents.

Once again, the latexes prepared with these nonionic surfmers are quite stable, versus addition of electrolytes, as well as versus freeze-thaw cycles. At room temperature, no change in the particle size is observed when the lattices are exposed to the 1M MgSO₄ solution. The critical flocculation temperatures (C.F.T.) are observed to be 62 and 66°C, respectively, for runs 4 and 7, while for the corresponding surfmers, the cloud points are 68 and 66°C, respectively. According to Napper,⁹ the stabilization can be considered to be

optimal when the cloud point is equal to the C.F.T. of the surfactant, which is the case for run 7. Moreover, the latex issued from run 7 is able to resist more than 10 freeze-thawing cycles at a solid contents of 10% and more than 20 at a solid contents of 0.1%, while that value is more than 5 for the latex from run 4.

CONCLUSIONS

In part IX of that series of articles, Schoonbrood and Asua³ defined the conditions for an optimal behavior of the reactive surfactant. Such compounds should not be too reactive at the beginning of the process; otherwise,

- (i) They can produce water-soluble polymers, with a possibility of bridging flocculation, and
- (ii) They can be consumed before the end of the process and so be buried inside the growing particles.

On the other hand, it is expected that they do react chiefly at the end of the process, so as to actually cover the surface of the particles, giving them stability. For that, it is necessary that their reactivity is well fitted with the reactivity of the main monomers.

The maleate compounds are thought to well correspond to the first condition, because they do not homopolymerize, and their reactivity toward the main monomers are rather moderate. At the end of the process, their reactivity is not well fitted, but this defect may be partly corrected, using a semicontinuous feed protocol of addition. Then, they are not too buried inside the particles and they can be, at least partly, located at the surface of the particles. In particular, the results obtained with the nonionic surfactants containing a long enough hydrophilic part, compensated by a high enough hydrophobic part (eventually using a CH₃ end group), show that good coverage is imported. This also results in good resistance to the freeze-thawing cycles, as well as good stability against the addition of electrolytes.

High solid content lattices are generally produced using a combination of ionic and nonionic surfactants. We believe that such a combination using a simple anionic maleate compound, such as HEC12, and a nonionic diester of the maleate derivative (as the one used for runs 6 and 7 of Table III) may be a useful formulation if associ-

ated to a seed and feed protocol. However, more reactive and hydrophobic surfactants, introduced at the very end of the feeding process, might also be a significant way to produce sterically stabilized particles by a grafted surfactant.

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